5618-MS-01.

(2)

Contract No. DAJA45-87-C-0058

"Electrically Conducting Organic Materials: Design, Synthesis and Characterization"

R&D # 5618 MS-01

Fourth Interim Report

July ,1989

Organic Metals Group
Department of Chemistry
Ben-Gurion University of the Negev
Beer Sheva 84105
Israel

Principal Investigators:

Prof. J. Bernstein
Prof. J.Y. Becker
Prof. S. Bittner
Prof. S.S. Shaik

Grant Administrator:

Mr. Moshe Amir, Director
Projects Administration Unit
Research and Development Authority
Ben-Gurion University
Beer Sheva, Israel

SUMMARY OF WORK AND CONCLUSIONS

Since our last interim report in February 1989, we have directed our efforts towards the syntheses and characterization of new materials which were outlined in the initial proposal. We are continuing to gain considerable experiience and expertise both in the synthetic methodology and in the ability to design electrically conducting organic materials. Our activities during the last six months continue to be in five main research areas:

a) Synthesis of D_2A type molecules

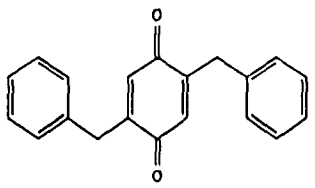
b) Synthesis of rigid A_2D type molecules

c) Electrochemical measurements and salt formation.

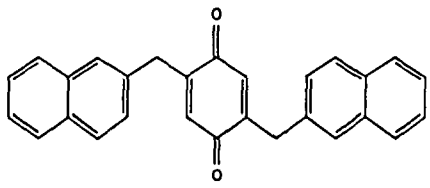
d) Synthesis of telluro derivatives of TTF

a. Synthesis of D_2A Type Molecules

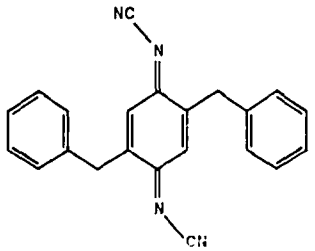
We have previously outlined the necessary conditions for conductivity in EDA complexes, and proved that D_2A type molecules (in which two donors and one acceptor are chemically bonded to one another) fulfill at least some of those conditions. In the course of the current reporting period we have continued with the synthesis of new molecules of this type. Thus, we prepared the two quinones **1** and **2** and coverted them to the corresponding dicyanimines **3** and **4**. These compounds are analoguos to the previously studied series of TCNQ derivatives and are expected to show similar electronic and structural properties. In addition, we have also prepared two brominated derivatives of **2**, namely **5** and **6**. We are currently preparing the dicyanimine derivatives of **5** and **6** and learning about the solid state packing properties of all the compounds **1-6**.



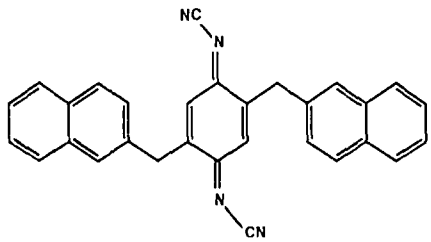
1



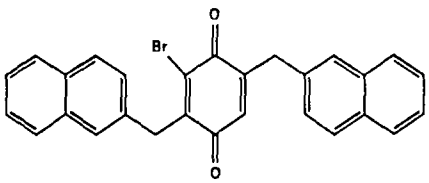
2



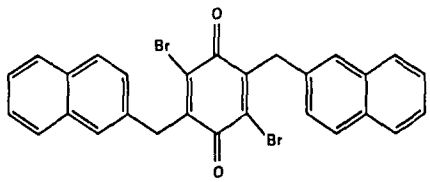
3



4



5

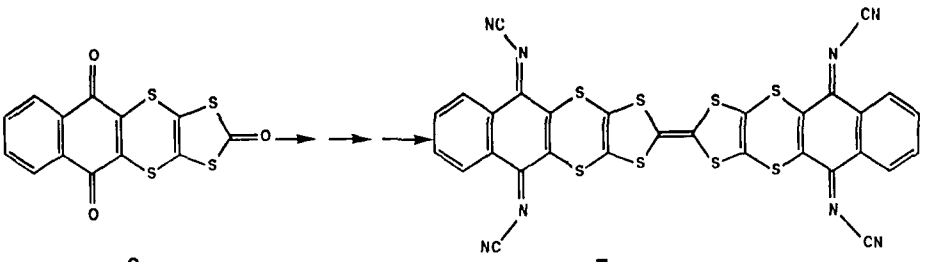


6

b. Synthesis of Rigid A_2D Type Molecules

As mentioned in our previous reports we are pursuing A_2D templates with sulfur atoms linking the moieties. some of those compounds exhibit a zig-zag type of stacking with considerable more overlap than usual. We felt that rigidizing the system and forcing it to planarity will increase the likelihood for aggregation in perfectly segregated stacks. Thus we are currently pursuing molecules of type **7** in which the donor is TTF and the acceptors are dicyanimine derivatives of naphtoquinone.

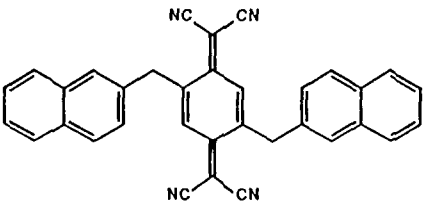
These syntheses proved to be considerably more difficult than we had thought. Thus far, after many time consuming experiments, we were able to prepare (in low yield) compound **8** which is a possible precoursor of **7** (after coupling and dicyanoimination).



8 7

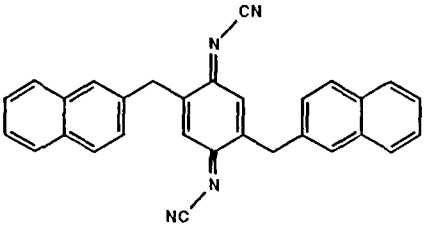
c. Electrochemical Measurements and Salt Formation

In the search for new organic conductors, it is convenient to match donors and acceptors by their electrochemistry. Cyclic voltametric data on some of the D_2A molecules are shown below. All experiments were carried out under argon in THF containing tetrabutylammonium tetrafluoroborate as electrolyte using platinum electrode as the working electrode and silver/ silver chloride as the reference. Currently we are measuring the electrochemical potential of all the other compounds described in this report.



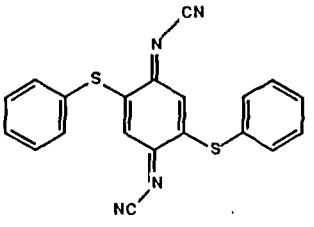
9

E1= +0.28V
E2= -0.35V



10

E1= +0.12V
E2= -0.56V



11

E1= +0.08V
E2= +0.17V
E3= +0.42V

Several EDA complexes and inorganic salts of **9**, **10** and **11** were prepared either by conventional or electrochemical ways. For example, we prepared the following materials based on **9**:

a) Potassium salt of **9**

b) Copper salt of **9**

c) TTF complex of **9**

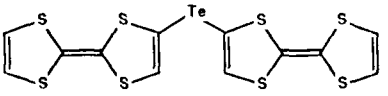
d) TMTSF complex of **9**

Those materials are currently under physical and spectral characterizations and we hope to report the results in the next semi - annual report.

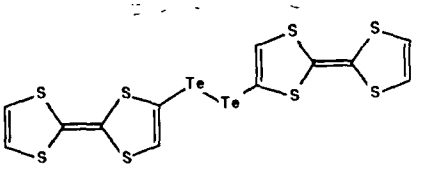
d. Synthesis of Telluro Derivatives of TTF

Te - TTF derivatives have attracted a great deal of attention because they are expected to further stabilize the metalic state of radical cation salts derived from them. Not less important are TTF - dimers which are promising donors for producing two-dimensional organic conductors.

We were able to synthesize two new compounds which are at the same time Te - TTF derivatives and TTF - dimers.

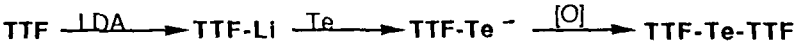


12 (TTF_2Te)

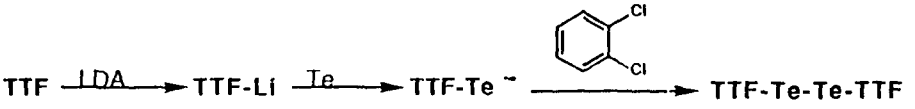


13 (TTF_2Te_2)

TTF_2Te was obtained in low yield by the following set of reactions :



TTF_2Te_2 was synthesized similarly using dichlorobenzen in the last step as an electron sink:



TTF_2Te_2 was obtained as a mixture of two polymorphic isomers. One as shiny black crystals ("black form") and the second as a red microcrystaline powder ("red form"). The crystal structure of both forms are now being determined by X-ray crystallography.

We are currently working on a revised synthesis of **12** and **13**, starting from bromo-derivatives of TTF. The starting material was already prepared according to the following scheme (together with the dibromo derivative) :

$$\mathbf{TTF} \xrightarrow{PhLi} \mathbf{TTF\text{-}Li} + \mathbf{TTF\text{-}Li_2} \xrightarrow{Cl_2BrC\text{-}CBrCl_2} \mathbf{TTF\text{-}Br} + \mathbf{TTF\text{-}Br_2}$$

The TCNQ salt of **13** were grown by diffusion methods in H-Type cells in CS_2. It was obtained as black shiny microcrystals. Its ir absorbtion (CN group) points to a ζ factor (partial charge transfer) of ~ 0.46. We are currently measuring the conductivity of the salt and studying its crystal structure.